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THERMAL CHARACTERIZATION AND FLAMMABILITY OF STRUCTURAL EPOXY ADHESIVE AND CARBON/EPOXY COMPOSITE WITH ENVIRONMENTAL AND CHEMICAL DEGRADATION

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Thermal Characterization and Flammability of Structural Epoxy Adhesive and Carbon/Epoxy Composite with Environmental and Chemical Degradation

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Abstract

This study investigates the thermal degradation and flammability properties of structural epoxy adhesive and carbon/epoxy composite subject to environmental and chemical agents typical of aerospace operations: water, jet fuel, hydraulic fluid, fuel additive (not mixed in jet fuel), at three conditioning temperatures similar to those experienced by an aerospace composite structure during its operation.

Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) gave results consistent with those from hardness tests on control and conditioned specimens: they provide evidence for the severity of the adhesive's degradation due to hydraulic fluid (for conditioning temperatures higher than room temperature) or fuel additive (at all temperatures of this study). TGA scans show the thermal degradation of carbon/epoxy composite by fuel additive at room temperature. Through Microscale Combustion Calorimetry (MCC), the flammability properties of selected specimens were measured. Results for the treatment at room temperature confirmed those from the TGA, DSC and hardness tests. The MCC showed a decreased heat release rate for the adhesive samples treated at high temperature in hydraulic fluid and fuel additive. This may be possibly due to the increased amount of char compared to the room temperature treatments.

These new results raise concerns regarding the durability of structural epoxy adhesive contaminated by hydraulic fluid or fuel additive, under simplified test conditions (no prior mechanical damage, no coatings/sealants, no mixing of fluids).

Keywords

Structural adhesive, durability, flammability, thermogravimetric analysis

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1. Introduction

Bonded joints made with polymer matrix composites are typically used in engineering applications where aspects such as low weight, smooth surfaces, and decreased risk for delamination are desired. Bonded joints are also adopted for repairs/retrofitting. Studies on their design, analysis and durability have been carried out for many years (e.g., [1–16]), since structural safety relies on bonded joints. Bonded and fastened joints "are perhaps the most common source of failure in aircraft structures" [17]. Because of the increased interest in adopting composite structures for primary loads in the aerospace, civil, naval, transportation and wind energy industries, it is important to investigate the durability of bonded joints during service. Improvements in joint durability would effectively prevent, delay and allow better monitoring of damage in the host structure due to thermo-mechanical fatigue, impact, environmental and chemical agents, manufacturing defects, overheating, or combinations of these factors.

In addition, polymeric matrix composites present a significant hazard due to their complex flammability behavior, which is driven by the resin's decomposition. Epoxies, the most common type of resin in aerospace applications [1], start decomposing between 350 and 600°C. The combustion process releases heat, soot and toxic fumes [18–21]. Glass and carbon reinforcements are non-flammable, but they will oxidize and produce inhalable particles. Fire retardant materials (for example, fire retardant epoxies, phenolic resins) may be used, but they still release smoke and fumes, and their cost is high. Moreover, the load-bearing capacity and the buckling strength decrease at temperatures as low as 100–200°C. The composite response to fire has been called "the single greatest impediment to the use of FRP composites in the design and construction of advanced ship systems and ship structures" [20]. We expect an impact on the structure's flammability, and consequently its resistance to fire, from any degradation mechanism affecting the polymeric resin. In this paper, we present thermogravimetric and flammability properties of structural epoxy adhesive and carbon/epoxy composite subject to environmental and chemical damages, which were caused by agents typical of aerospace service: water, jet fuel, fuel additive, hydraulic fluid. First, gravimetric tests were conducted at room temperature (approximately 22°C), and at two high temperatures compatible with those of an aerospace composite structure in service: 70 and 85°C. As a first approximation, simplified laboratory test conditions were applied: no prior thermo-mechanical damage, no coatings, no combinations of fluids (e.g., fuel additive was not mixed in jet fuel). The individual components of a bonded joint were examined based on results from a preliminary study on lap joints [22]. We expect to extend the study to actual lap joints in the future.

As shown in [22], distinct irreversible chemical degradation, evidenced also by Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) tests, was encountered when the structural adhesive was treated in anti-icing additive or hydraulic fluid. Other treatments seemed to be much less detrimental to the adhesive. Carbon/epoxy composite, on the other hand, was impacted at a much

lesser rate, and only by fuel additive at room temperature. Microscale Combustion Calorimetry (MCC) tests were conducted to characterize the flammability behavior of control and conditioned samples. The heat release rate results are consistent with the TGA scans for the room temperature treatment. At higher temperatures, the heat release rate decreases. This may be due to the increased amount of char residue present in the conditioned specimens.

Methods are discussed in Section 2, while results are presented and discussed in Section 3. Section 4 summarizes the findings of this study.

2. Experimental

Specimens made with either epoxy structural adhesive or woven carbon/epoxy were prepared and tested in a variety of conditions, as reported in [22]. Some selected samples were sent for the DSC/TGA and microcalorimetry tests, the focus of this paper, after the conditioning tests were completed.

2.1. Materials and Methods

2.1.1. Structural Adhesive

The adhesive used in this study was Hysol® EA 9360 (Loctite/Henkel, Düsseldorf, Germany), a two-component toughened paste adhesive with high peel strength and room temperature storage. It is used for aerospace maintenance, repairs and operations (MRO), and its published service temperature is 107–121°C [23, 24]. The service temperature is defined by the manufacturer as the temperature at which the adhesive still retains a tensile lap shear strength equal to 6.9 MPa using test method ASTM D1002.

Specimens (Fig. 1) were prepared following ISO 62 standard, with dimensions 60 mm × 60 mm × 1 mm for ease of fabrication, and ASTM D5229 for the rest of the procedure [22]. No primers/coatings and no mechanical damage (abrasion, static/fatigue/impact loading, etc.) were applied. Five specimens per condition were

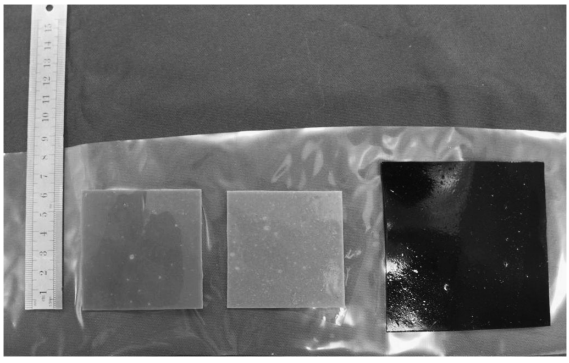

Figure 1. Adhesive specimens conditioned in (left) water at 70°C, (center) hydraulic fluid at room temperature, (right) hydraulic fluid at 70°C. The specimens on the left and at the center have approximate size equal to 60 mm (the initial/nominal size is 60 mm).

immersed in enclosed containers of the following unmixed liquids: (a) fresh water, (b) jet fuel, (c) Prist® Hi-Flash™ fuel additive (Prist Aerospace Products, Conroe, TX, USA) and (d) Skydrol® 500B hydraulic fluid (Solutia, St. Louis, MO, USA). The fuel additive was diethylene glycol monomethyl ether, which is typically mixed with jet fuel to prevent freezing. For sake of simplicity, the fuel additive in the current project was not combined with jet fuel, hence its concentration is not representative of actual operations. Previous researchers, Rider and Yeo [25], studied the effects of this chemical on adhesive joints, at a concentration four times greater than the nominal concentration. Rider and Yeo showed the presence of "massive disbonds" in adhesive joints (up to 75% of bonded area).

The hydraulic fluid was a phosphate ester-based fluid with enhanced heat resistance. This type of chemical has been shown to attack paints, sealants and resins in aerospace composites [1], and to possibly cause delamination between the honeycomb core and fiberglass composite skin in the rudder surfaces of some Airbus A300 aircraft [26].

Three different conditioning temperatures were used: room temperature (22°C), 70°C (in a safety oven, model VWR 1330, from VWR International, Radnor, PA, USA), and 85°C (in a furnace/oven Series 3710 from Wagner Instruments, Burien, WA, USA). The tests lasted approximately three years, with very limited interruptions. The 70 and 85°C temperatures are reasonable values for the operation of aerospace composite structures. For example, "Jet fuel is a fluid that will always be in contact with the composite on a long term basis and at elevated temperatures" (121 and 177°C in the work of Curliss [27]). The temperature of 70°C is "a typical temperature that an aircraft surface could reach on the ground due to solar heating" [28].

To understand the relation of these treatment temperatures with the adhesive glass transition temperature, T_g, one should consider the requirement of the ASTM D5229 for gravimetric tests to be done at least 25°C below the material T_g. The manufacturer's recommendation is to cure at room temperature for 5 to 7 days "to achieve normal performance" [24]. In addition, the adhesive specifications state that "Accelerated cures up to 93°C (for small masses only) may be used as an alternative. For example, 1 h at 82°C will give complete cure".

Due to the dependence of T_g on the polymer's state of cure, test type and heating rate during the test, the service temperature was utilized as a ceiling for the selection of the temperatures in the treatment.

Post-curing (two hours at 82°C) was applied to a small group of adhesive specimens (indicated from now on as "complete cure" specimens), while the non-post-cured specimens are described as "normal cure" specimens (for "normal performance" [24]). It is assumed that post-curing may not be easily applicable in some situations (e.g., manufacturing or repair of large composite or metallic/composite structures). Further discussion on the glass transition temperature of the adhesive follows in Section 3.

Due to the geometry needed for the gravimetric tests, tensile tests were not feasible on the available equipment. Hardness tests were preferred instead, and mechanical degradation was inferred from the decrease of hardness with respect to baseline hardness. The conversion between hardness and tensile strength was calculated through statistical methods including boxplots and locally weighted scatterplot smoothing (see [22] for details). Tensile strength, not shear strength, was used as the property of choice to extrapolate the extent of mechanical degradation due to conditioning in those contaminants.

2.1.2. Carbon/Epoxy

The carbon/epoxy specimens were fabricated with Vacuum Assisted Resin Transfer Molding (VARTM), with ten layers of as-received carbon T-300 plain weave (weight/area 98.3 g/m^2, Sigmatex, Benicia, CA, USA) and Proset® LV 117/237 (Proset, Bay City, MI, USA), with final dimensions 100 mm × 100 mm × 1 mm, as per ASTM D5229 standard. The cure cycle consisted of 4 h at 50°C and 16 h at 60°C. The material properties of a single lamina are: longitudinal modulus E_{11} = transverse modulus $E_{22} = 48.4 \pm 3.71$ GPa; in-plane shear modulus $G_{12} = 2.685 \pm 0.198$ GPa; major in-plane Poisson's ratio $v_{12} = 0.0380 \pm 0.0153$. Specimens were conditioned in the same fluids as above, at room temperature (all conditioning liquids) and at 70°C (all conditioning liquids except jet fuel).

2.2. Differential Scanning Calorimetry and Thermogravimetric Analysis

Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) were carried out with a Netzsch Thermogravimetric Analyzer/Differential Scanning Calorimeter (TGA/DSC) Model STA 409 PC, with Al_2O_3 pans and lids. The temperature for all samples varied from room temperature (approximately 22°C) to 900°C, at a rate of 15°C per min. All samples were processed under a nitrogen purge of 50 ml/min. The samples were shipped from UC Davis (California, USA) to Tyndall Air Force Base (Florida, USA) after the three years test period, and they were pre-conditioned prior to the DSC/TGA tests.

2.3. Microscale Combustion Calorimetry

Microscale Combustion Calorimetry (MCC) was performed to determine the burning characteristics of the adhesive and composite samples. This test was developed by the US Federal Aviation Administration (e.g., Lyon and coworkers [29–31]), standardized by ASTM (with ASTM D7309-07), and adopted recently by other authors, e.g., Xing *et al.* [32] and Lu and Wilkie [33].

Compared to cone calorimeter tests, MCC has many advantages: a controlled small-scale test environment in which to carry out thermal decomposition, small (milligram-sized) samples, and a limited amount of time to perform experiments (on the order of 5 min). Most importantly, the MCC has the ability to provide results that are intrinsic properties of the material, and independent of environment, sample size and orientation. However, phenomena such as dripping, swelling, charring limit the effectiveness of the method. The MCC analysis consists of separating pyrolysis

from oxidation of the volatiles coming from the solid sample. The temperature is ramped at a constant rate (1°C/s) to heat the samples under inert (N_2) conditions (80 ml/min) to a maximum temperature of 750°C. The volatiles are then introduced into the combustion chamber where the gases (added O_2 at 20 ml/min) oxidize them.

In the current work, small (approximately 5 mg) samples were cut from random locations of the control and treated (fuel additive, hydraulic fluid, jet fuel, and water) adhesive and carbon/epoxy samples. Samples were placed in ceramic cup holders and weighed before and after (for most runs) the MCC analysis. There were 4 or 5 samples per condition.

Heat release rate, *HRR*, is considered "the single most important variable in fire hazard" [34], and is calculated from oxygen consumption [35]. The test method is clearly defined by ASTM D7309-07. The heat release capacity, η_c, is a key flammability parameter obtained through this test only, and calculated by dividing the maximum specific *HRR* by the heating rate (1°C/s). Heat release capacity may be related to other flammability parameters typically obtained by cone calorimetry, for example limiting oxygen index (LOI%), and the *HRR* at a 50 kW/m^2 external flux [30]. The total heat release is determined by integrating the heat release rate *versus* the time curve. The heat release temperature is the specimen temperature corresponding to the maximum *HRR*, while the char/fiber residue is the ratio of the sample final mass and the sample initial mass.

3. Results and Discussion

3.1. Mass Uptake and Hardness

Changes in mass uptake and hardness are reported in [22] and [36], and are here summarized for the sake of completeness, and for comparison with the thermal degradation and flammability results. Table 1 shows the mass uptakes of structural adhesive and carbon/epoxy specimens, measured with a Mettler balance (100 g range, 0.1 mg resolution). We emphasize the considerable mass uptake for adhesive specimens in fuel additive and hydraulic fluid, at temperatures above room temperature. By comparison, the literature shows mass gains of ∼9% for epoxy in water [37], and only 4.1% for carbon/epoxy woven specimens in deionized water at 60°C [38].

Hardness could not be measured reliably for specimens conditioned in fuel additive at 70 and 85°C, as the specimens broke into pieces. For the hydraulic fluid treatment, relative hardness decreased by about 50% at 70 and 85°C. There was no statistically significant change for water and jet-fuel treatments (only up to ∼2%). Figure 2 shows Shore D hardness values for adhesive samples at 70 and at 85°C (more information can be found in [22]).

For the carbon/epoxy specimens, relative hardness variations were insignificant for all conditions except for fuel additive treatment (decreased by 12.5% with respect to the baseline, for room temperature conditioning). Although mass uptake is

Table 1.
Mean ± one standard deviation of the mass uptake in each tested condition. 'RT' stands for room temperature

Material in conditioning fluid	Temperature, cure stage (for adhesive only)	Final mass gain (%)
Adhesive in water	RT, normal cure	7.187 ± 0.0845
	70°C, normal cure	5.798 ± 0.2306
	85°C, normal cure	5.601 ± 0.1597
Adhesive in fuel additive	RT, normal cure	37.70 ± 0.5256
	RT, complete cure	30.54 ± 0.9748
	70°C, normal cure	83.95 ± 4.125
	70°C, complete cure	65.93 ± 2.498
	85°C, normal cure	84.95 ± 3.313
Adhesive in hydraulic fluid	RT, normal cure	0.1353 ± 0.0257
	70°C, normal cure	130.6 ± 24.24
	85°C, normal cure	165.8 ± 11.31
Adhesive in jet fuel	RT, normal cure	0.3277 ± 0.1875
	RT, complete cure	0.3628 ± 0.0404
	85°C, normal cure	7.662 ± 0.0618
Carbon/epoxy in water	RT	0.9361 ± 0.0438
	70°C	1.595 ± 1.541
Carbon/epoxy in fuel additive	RT	11.51 ± 2.770
	70°C	11.43 ± 0.3450
Carbon/epoxy in hydraulic fluid	RT	0.3392 ± 0.1790
	70°C	2.037 ± 0.0274
Carbon/epoxy in jet fuel	RT	0.2361 ± 0.0147

comparable for fuel additive treatment at room temperature and at 70°C, the gravimetric tests were stopped after 360 days at room temperature, while mass uptake still increased. At 70°C, sorption of fuel additive reached steady-state in 25 days.

Microscopy (with a Hitachi TM-1000 microscope) on selected adhesive specimens treated at 70°C showed the presence of irreversible degradation due to hydraulic fluid and fuel additive [22].

The hardness changes are consistent with the DSC and TGA outcomes, as shown in Section 3.2.

3.2. Glass Transition Temperature and Thermal Degradation

The control and conditioned adhesive samples were characterized by DSC and TGA tests. Part of the outcome of these tests is already discussed in a book chapter [36]. This section is meant to present these findings to a wider research audience, to add some new results from DSC and TGA tests (not published in [36]), and to correlate them with the new MCC tests that follow.

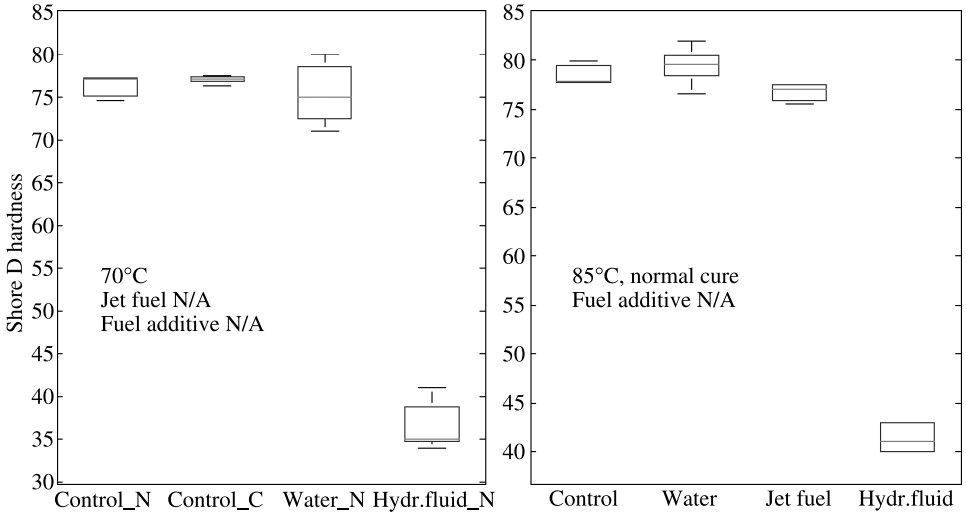

Figure 2. Shore D hardness results for control and conditioned adhesive specimens at 70 and 85°C. In the 70°C tests, '_N' and '_C' indicate, respectively, normal and complete cures. Fuel additive specimens were so degraded that hardness could not be measured reliably.

One sample only per condition was tested. It is assumed that the variability in the results parallels the scatter in the hardness test results [22], which can also be observed in Fig. 2 for selected samples. The DSC tests showed that the service temperature of 107°C was approximately 40°C above the transition point (possibly the T_g itself) of the baseline adhesive samples at room temperature, Table 2. The post-cured control adhesive typically had a higher T_g, consistent with the higher hardness [22], but T_g was still below the service temperature. Control specimens prepared with normal cure and then tested at 70 and at 85°C exhibited a transition behavior (possibly a T_g range) which was close to that of the post-cured specimens, and mirrored the hardness behavior of the control specimens [22]. In particular, the control specimens at 70°C had statistically equivalent Shore D hardness at the two different cures (normal and complete), Fig. 2. This is reflected by a relative difference in the inflection points $\frac{IP_{85}-IP_{70}}{IP_{70}} \times 100$ (in Table 2) of ∼2.5%.

On the other hand, the T_g of the control specimens conditioned at 85°C was expected to be higher than the T_g of the control specimens conditioned at 70°C. In fact, the Shore D hardness (SDH) boxplot (Fig. 2) shows a slight hardness increase for the 85°C batch (the relative difference in the medians, $\frac{\text{median}(\text{SDH}_{85})-\text{median}(\text{SDH}_{70})}{\text{median}(\text{SDH}_{70})} \times 100$ is ∼1%), while the relative difference in the inflection points in Table 2 is −7%.

Conditioning in water led to a small decrease of the transition range of the epoxy adhesive at both 70 and 85°C with respect to the control at those temperatures, in line with the well-known plasticization of epoxy (e.g., [39]). The hardness tests show statistically similar values at these high temperatures, Fig. 2. On the other hand, experimental results are somewhat ambiguous for treatment in water at room temperature, as plasticization was expected (Table 2). However, the higher T_g of

Table 2.
DSC data for structural adhesive (at a rate of 15°C/min). 'RT' stands for room temperature

Treatment/cure type/test temperature (°C)	Transition range (°C)
Control/normal/RT	onset 59, peak 65.5
Control/complete/RT	onset 87.0, inflection 92.0
Control/normal/70	onset 95.2, inflection 101
Control/complete /70	onset 93, inflection 98.5
Control/normal/85	onset 83.5, peak 92.0
Water/normal/RT	onset 77.5, peak 86.4*
Water/normal/70	onset 84.6, inflection 90.0
Water/normal/85	onset 87.5, inflection 91.3
Hydraulic fluid/normal/RT	onset 91.1, inflection 94.7
Hydraulic fluid/normal/70	N/A (data not conclusive)
Hydraulic/normal/85	onset 76.5, peak 110.8
Fuel additive/normal/RT	onset 55.0, peak 63.0
Fuel additive/normal/70	onset 84.1, peak 119.2
Fuel additive/normal/85	onset 65.1, peak 98.6
Jet fuel/normal/RT	onset 51.3, peak 57.3
Jet fuel/complete/RT	onset 88.7, inflection 91.2
Jet fuel/normal/85	onset 81.6, inflection 84.5

* There is a potential transition zone around 50°C. However, the region in high 70–mid 80°C is more significant.

the water-conditioned specimens at room temperature is consistent with the higher hardness of these specimens (Fig. 8 in [22]).

Immersion in fuel additive at 70 or at 85°C decreased the transition point/T_g. Hardness measurements could not be carried out due to the specimens' high level of degradation. From [22], it is evident that the gravimetric curves at 70 and at 85°C do not have the same trend/slope, hence different diffusion-controlled reaction mechanisms are taking place. For example, in the 85°C treatment, the sorption was more significant (see Table 1) and in much shorter time (230 days *versus* the 553 days in the 70°C treatment).

On the other hand, the hydraulic fluid treatment increased the T_g, possibly due to chemicals in the hydraulic fluid that led to anti-plasticization chemical reactions. This result appears to contradict the drop in hardness shown in Fig. 2 and the TGA results below, and will be investigated in the future.

Jet fuel conditioning seems to increase the T_g of the adhesive at high temperatures. However, hardness variations were statistically insignificant with respect to the control specimens at the same temperature.

Regarding the Pro-set® epoxy in the carbon/epoxy samples, its T_g at room temperature was in the 60–70°C range (onset at 63.4°C, peak at 77.5°C). Hardness boxplots in [22] feature statistically equivalent behaviors for all treatments, except

fuel additive. As mentioned above, the carbon/epoxy specimens gained approximately the same mass of fuel additive, but the gravimetric tests exhibit a marked increasing slope after 360 days, and this does not occur in the 70°C treatment (mass uptake reached equilibrium within 25 days). Also the TGA results below indicate that the room temperature conditioning in fuel additive was more detrimental, notwithstanding the fact that room temperature is well below the T_g of the neat epoxy.

At all temperatures, the TGA tests showed that the control samples (with normal and complete cures at room temperature and at 70°C, normal cure only at 85°C) had a similar behavior, showing a ∼5–10% mass loss up to 350°C, a rapid drop in mass loss between 350 and 500°C, and a small additional mass loss (∼2–3%) between 500 and 900°C. The residual mass for control samples ranged between 12% (normal cure) and 18% (complete cure), Table 3. Residual mass from the MCC tests is also given in this table, and will be further commented upon in Section 3.3.

At room temperature, the results for the adhesive control and treated samples had similar profiles, except for the fuel additive sample, whose mass loss occurred at a faster rate up to 350°C, Fig. 3.

Treatments in water or jet fuel caused only small variations in the TGA profiles, even though exposure occurred for long periods of time and at high temperatures (e.g., 85°C for 1250 h). The mostly unchanged TGA profiles indicate no significant chemical or structural changes to the material due to a median mass gain up to 7% (for water) and ∼8% (for jet fuel), Table 1.

Regarding the hydraulic fluid and the fuel additive, the TGA scans showed major differences between treatments at room temperature and at high temperatures, Figs 4–6. In particular, for hydraulic fluid treatment, the gravimetric tests show insignificant mass uptake at room temperature, in contrast to the behavior at 70 and 85°C. At these temperatures, a mass loss increase with temperature clearly appears in the TGA scans, in particular a 40% loss at only 200°C. Comparison with the neat hydraulic fluid shows no volatilization of the fluid alone at 200°C, Fig. 5.

As far as the treatment with fuel additive alone (no mixing with jet fuel), the TGA scans indicated that this fluid alone is actually more detrimental than the hydraulic fluid, Figs 4, 6. Not only the mass loss at the higher temperatures was more pronounced, but also this fluid affected the adhesive already at room temperature (Figs 3, 6). The effect at room temperature is consistent with the gravimetric tests, where a ∼38% (for normal cure) median mass uptake was recorded (Table 1). Postcuring of the adhesive reduced the impact of fuel additive.

For the carbon/epoxy specimens, TGA plots demonstrated that the fuel additive had an impact only at room temperature, leading to approximately 10% more mass loss (Fig. 7). This outcome is similar to the larger hardness changes at room temperature than at 70°C discussed above and in [22].

Table 3.
Residual masses from TGA and MCC tests, in percents. Treatments not available are not shown. 'RT' stands for room temperature

Treatment	RT conditioning		70° conditioning		85° conditioning
	Complete cure	*Normal cure*	*Complete cure*	*Normal cure*	*Normal cure*
Adhesive					
Control					
TGA	17.0	12.3	14.8	18.0	–
MCC	11.1	10.7 ± 1.65	11.3 ± 1.17	12.0 ± 1.14	13.1
Fuel additive					
TGA	12.0	13.3	14.2	11.0	13.9
MCC	9.41 ± 1.77	–	13.8 ± 1.14	15.5 ± 1.26	–
Hydraulic fluid					
TGA	–	12.9	–	15.0	13.7
MCC	–	10.3 ± 1.80	–	15.3 ± 1.64	16.6 ± 5.81
Jet fuel					
TGA	14.7	12.8	–	–	14.7
MCC	13.9 ± 2.76	11.7 ± 1.80	–	–	12.1 ± 6.76
Water					
TGA	–	13.0	–	9.11	13.8
MCC	–	20.4 ± 6.90	–	11.6 ± 0.999	13.1 ± 0.722
Composite					
Control					
TGA	61.6		64.2		
MCC	53.3 ± 4.12		–		
Fuel additive					
TGA	54.8		–		
MCC	–		–		
Hydraulic fluid					
TGA	62.0		60.7		
MCC	–		–		
Water					
TGA	62.6		64.2		
MCC	–		–		

3.3. Flammability

From the O_2 consumption by the volatile materials in the solid, the heat release rate (*HRR*) is determined, and is shown in Figs 8–10. Maximum *HRR* values are presented in Table 4.

3.3.1. Room Temperature Treatment

MCC results from most conditioned samples were very similar to the baseline samples, for both adhesive and carbon/epoxy samples, at room temperature, Table 4, Fig. 11. The only noticeable difference is with the fuel additive treatments

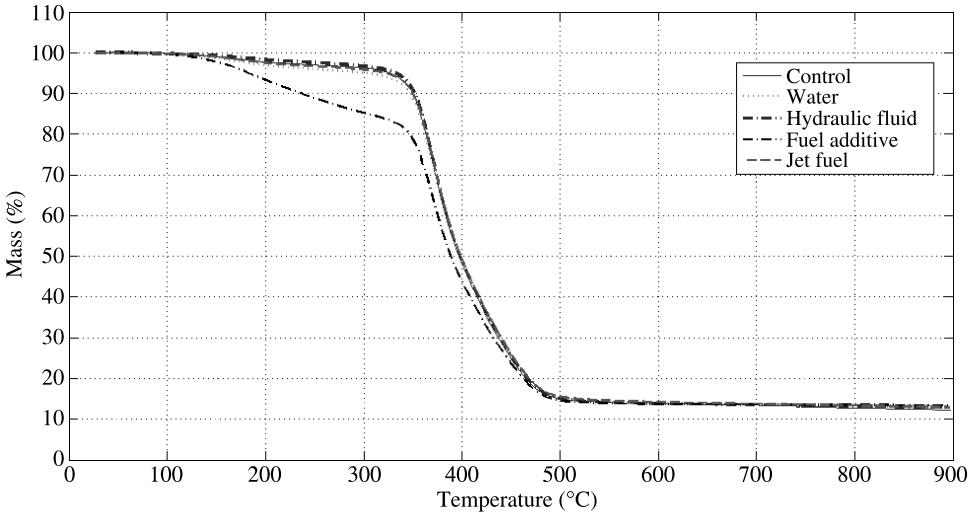

Figure 3. TGA results for control and conditioned adhesive at room temperature [36].

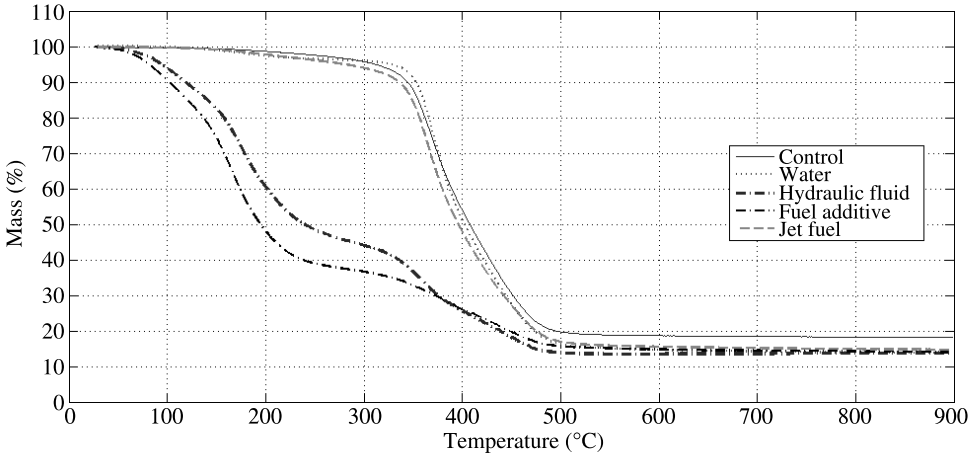

Figure 4. TGA scans of control and conditioned adhesive specimens, at 85°C [36].

for both the adhesive and composite, which have a small peak in the 150–250°C range (Fig. 8), due to low molecular weight gases that may have been physically adsorbed onto the epoxy adhesive (i.e., not chemically bonded to the solid). This decomposition at these relatively low temperatures could give rise to structural instability or possibly structural failure, if the material were exposed to a heat source. The trend is very much consistent with the outcome from the gravimetric and TGA tests (all samples gave similar profiles, except for those treated in fuel additive). In the fuel additive samples, there was a heat release of 1.8 ± 0.2 kJ/g during the low-temperature peak mentioned above (between 150–250°C). The combination of both

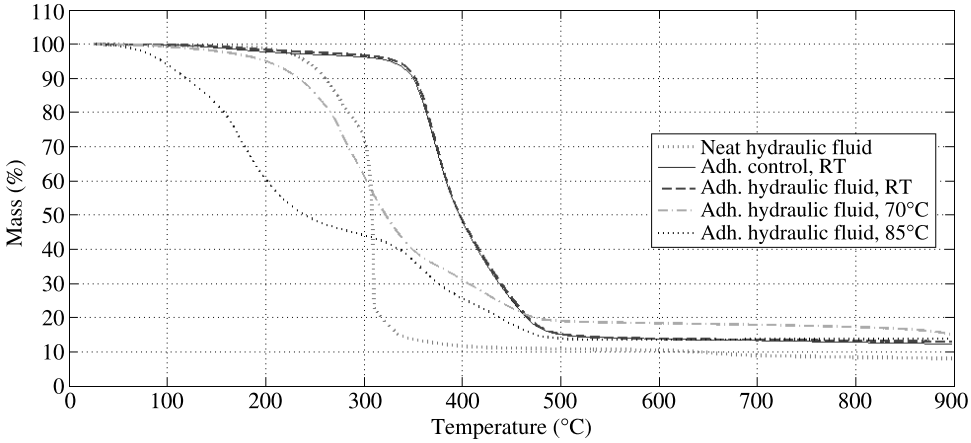

Figure 5. TGA scans of neat hydraulic fluid, control adhesive specimen, and conditioned adhesive specimen in hydraulic fluid, at room temperature, 70 and 85°C (no post-cure) [36]. 'RT' stands for room temperature.

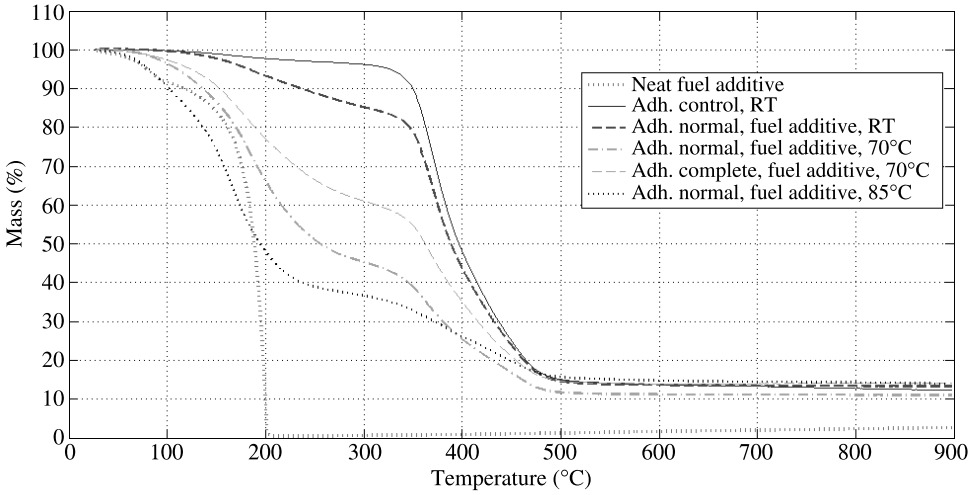

Figure 6. TGA scans of neat fuel additive, adhesive control specimen, and adhesive specimen treated in fuel additive [36]. Type of curing ('normal', 'complete') is also indicated. 'RT' stands for room temperature.

low- and high-temperature peaks would approximately equal the amount of energy released during the main peak of the *HRR* curves obtained from other treatments.

The adhesive's *HRR* peak has an inflection (Figs 8 and 9) which shows a distinct region (420–470°C) due to higher molecular weight volatiles released from the solid. Pyrolysis (neglecting early decomposition peak for fuel additive samples) of the adhesive samples began around 300–320°C, and ended at approximately 520°C,

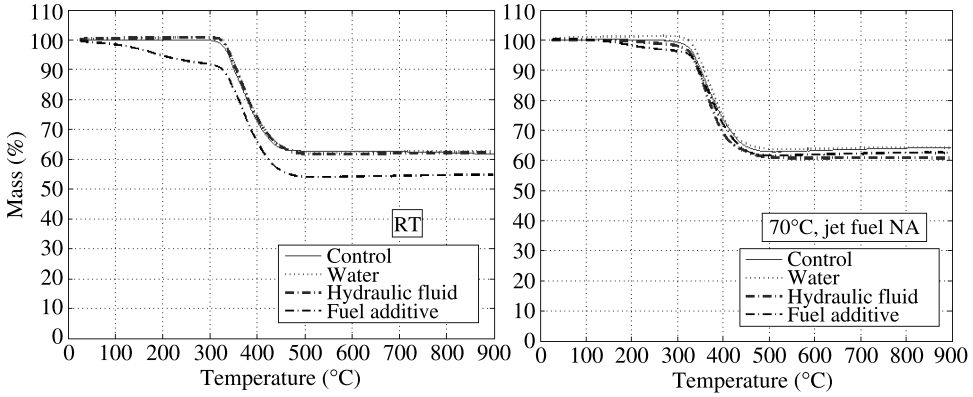

Figure 7. TGA scans of carbon/epoxy control and conditioned specimens at room temperature ('RT') and 70°C [36]. Jet fuel-treated specimens were not available for these scans.

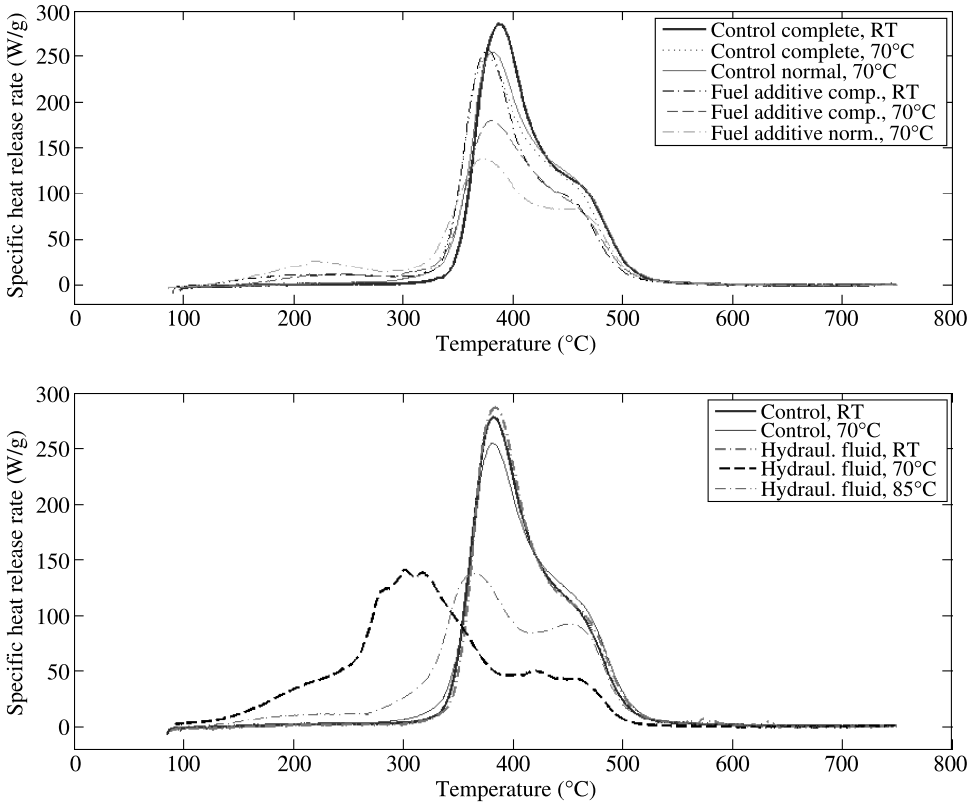

Figure 8. Specific heat release rates of representative control and conditioned adhesive samples: (top) fuel additive treatment, (bottom) hydraulic fluid treatment.

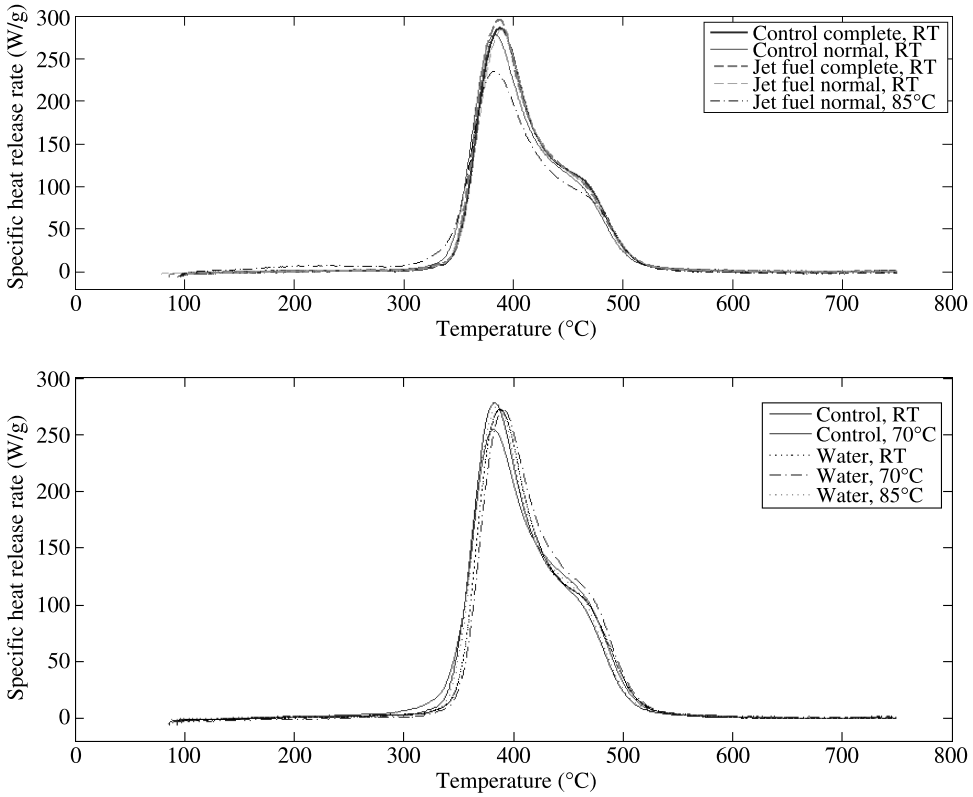

Figure 9. Specific heat release rates of representative control and conditioned adhesive samples: (top) jet fuel treatment, (bottom) water treatment.

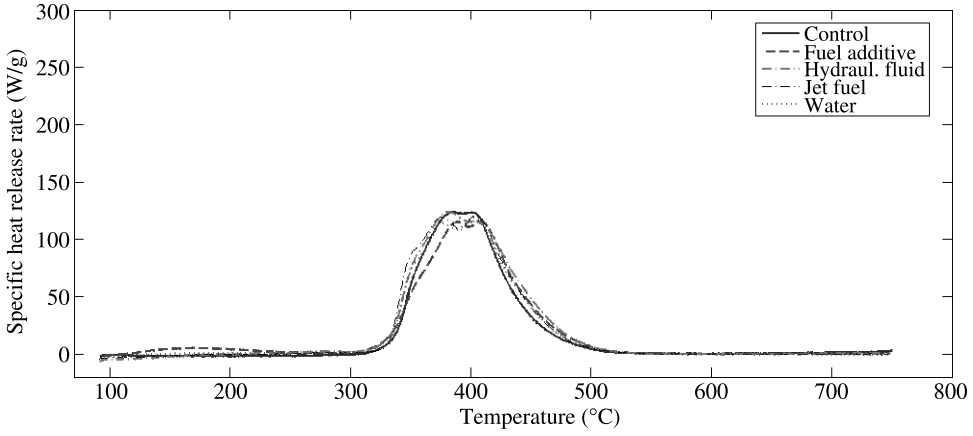

Figure 10. Specific heat release rates of representative control and conditioned carbon/epoxy samples at room temperature.

Table 4.
Maximum heat release rate *HRR* (W/g) for control and conditioned specimens, expressed as average ± one standard deviation. 'RT' stands for room temperature

Treatment	RT conditioning		70° conditioning		85° conditioning
	Complete cure	*Normal cure*	*Complete cure*	*Normal cure*	*Normal cure*
Adhesive					
Control	284 ± 18.4	288 ± 9.03	243 ± 7.78	261 ± 27.2	–
Fuel additive	255 ± 19.8	–	180 ± 3.60	137 ± 4.38	–
Hydraulic fluid	–	292 ± 15.7	–	130 ± 14.8	138 ± 8.96
Jet fuel	297 ± 18.9	280 ± 13.2	–	–	240 ± 3.49
Water	–	275 ± 18.4	–	268 ± 7.41	276 ± 6.09
Composite					
Control		131 ± 9.27		–	
Fuel additive		120 ± 8.04		–	
Hydraulic fluid		115 ± 10.3		–	
Jet fuel		119 ± 4.95		–	
Water		125 ± 7.97		–	

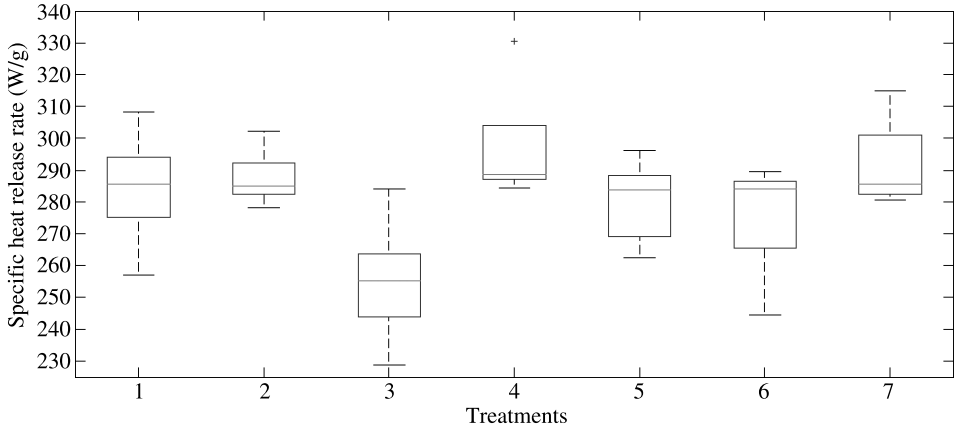

Figure 11. Boxplots of specific heat release rates for control and conditioned adhesive samples treated at room temperature. Legend: 1 = control C; 2 = control N; 3 = fuel additive C; 4 = jet fuel C; 5 = jet fuel N; 6 = water N; 7 = hydraulic fluid N. 'N' = normal cure, 'C' = complete cure.

except for the specimens conditioned in hydraulic fluid at 70 and 85°C, as will be discussed later.

For the carbon/epoxy samples, pyrolysis began at approximately 305°C and ended at 510°C, Fig. 10. The carbon/epoxy *HRR* curve typically has a double peak, the first at approximately 375°C, the next at 410°C. Since most of the carbon fibers do not pyrolyze, the fibers may create a substrate or pseudo-catalyst, which allows

the higher molecular weight (420–470°C) gases to be released at a lower temperature (410°C). Most likely, however, it is due to the difference in chemical makeup between the structural adhesive (epoxy Hysol® EA 9360) and the epoxy resin (Proset® 117 LV/237) of the composite.

From Table 4, there is only little variation among the adhesive samples with normal cure at room temperature. The complete cure fuel additive treatment showed a slightly lower energy release than all other normal cure treatments. At room temperature, the carbon/epoxy samples exhibited mostly similar energy release. However, jet fuel samples showed slightly higher energy release when compared to other composite configurations, possibly due to high energy content of jet fuel. Void spaces from processing the composite may allow for jet fuel to adsorb onto the solid, while the adhesive may have reduced void spaces due to the presence of an additional clamped caul plate during its manufacturing[1] (Fig. 3, [22]). Thus, no increase in energy release was observed for the jet fuel treated adhesive. To statistically validate this claim, more experiments would have to be performed.

At room temperature, adhesive samples after pyrolysis retained $12 \pm 4\%$ of their mass, composed mostly of char. Composite samples retained $53 \pm 4\%$ of their mass, composed mostly of undamaged carbon fibers as well as char from the epoxy resin. Measured residual masses following the experiment were similar to TGA values, Table 3.

3.3.2. High Temperature Treatments

Pyrolysis started and ended approximately at the same temperatures as in Section 3.3.1, except for the hydraulic fluid: in this latter case, it started at average temperatures of, respectively, 130°C (for the 70°C samples) and 273°C (for the 85°C samples), and was over at, respectively, 470 and 538°C. At higher temperatures, the fuel additive and hydraulic fluid conditioned adhesive samples exhibited a reduced *HRR* (more marked in the hydraulic fluid case), and a shift to the left of the heat release temperature (Fig. 8).

The *HRR* curve of the hydraulic fluid treatment at 70°C is counterintuitive with respect to the TGA plots: in fact, the TGA plot showed the 85°C treatment, not the 70°C treatment, to be the worst case among the three conditioning temperatures. The physical aspect of the adhesive samples treated in hydraulic fluid suggests that different types of diffusion-controlled reactions took place at these two high temperatures. When the gravimetric tests were stopped, the specimens treated at 70°C were black and leathery, while those treated at 85°C had a dark green color, and appeared to harden upon cooling. During the MCC tests, the samples conditioned at 70°C swelled, with the formation of a bubble-like black char. Samples treated at 85°C had no observable swelling and their color blackened during the pyrolysis. The lack of swelling in these latter specimens shows that volatiles did not escape

[1] A caul plate is a metallic plate that may be used to apply uniform pressure during composite manufacturing. It was required in the fabrication of the adhesive samples because of the 1 mm thickness requirement.

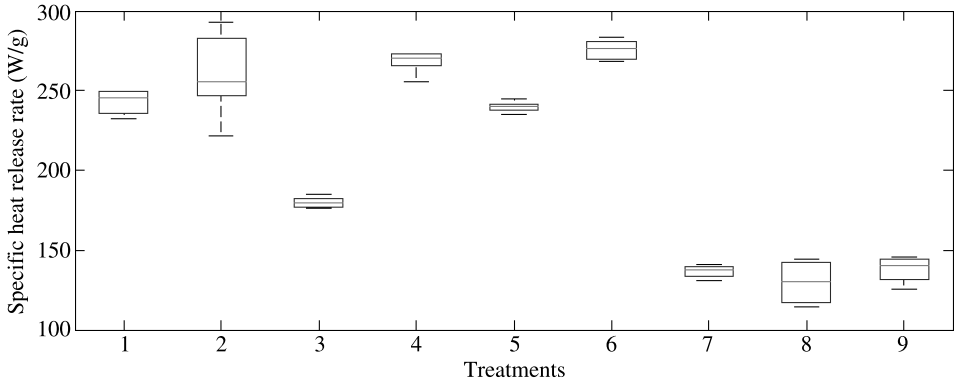

Figure 12. Boxplots of specific heat release rates for control and conditioned adhesive samples treated at 70 and 85°C. Legend: 1 = control C, 70°C; 2 = control N, 70°C; 3 = fuel additive C, 70°C; 4 = jet fuel N, 85°C; 5 = water N, 70°C; 6 = water N, 85°C; 7 = additive N, 70°C; 8 = hydraulic fluid N, 70°C; 9 = hydraulic fluid N, 85°C. 'N' = normal cure, 'C' = complete cure.

from the surface of the solid as quickly as for the other samples. It is possible that the samples' storage conditions between the end of the gravimetric tests and the MCC tests might have influenced the *HRR* outcome. However, the mass uptake from the tests, reported in Table 1, clearly shows the presence of different degradation mechanisms between the 70 and the 85°C treatments, which, in our opinion, contributes to explain the behavior in Fig. 8.

Maximum *HRR* values were noticeably lower for hydraulic fluid and fuel additive treatments, Table 4, Fig. 12. This was unexpected, because of the outcome of gravimetric tests, hardness tests, DSC and TGA scans, showing the presence of irreversible degradation and possibly an increased fire risk.

We should point out the different heating rates between the two tests (15°C/min in the TGA, 60°C/min in the MCC), which could cause increased cross-linking of the carbon atoms present in the tested materials, and, thus, increased charring. Also, one other possible explanation for this phenomenon may be the considerable increase of average residual mass (Table 3) at higher temperature: there is a relative change, $\frac{(m_{\mathrm{f,HT}}-m_{\mathrm{f,RT}})}{m_{\mathrm{f,RT}}} \times 100$, up to a 65% increase for the fuel additive case (normal cure, 70°C treatment) and, for the hydraulic fluid case, 49% increase (normal cure, 70°C treatment), and 61% increase (normal cure, 85°C treatment). This means that more char was produced by the end of the pyrolysis, which affected the flammability behavior in a nonlinear manner, and obstructed heat and mass transport. In view of the strong evidence for degradation at higher temperatures, provided by the other tests (Sections 3.1–3.2), additional work may be needed, possibly with a cone calorimeter. MCC analysis assumes complete combustion, but phenomena like charring may lead to ambiguous results, as observed not only in the current case, but also by Lyon *et al.* [31], in flame retardant plastics. In our MCC tests, there was only N_2 in the pyrolysis chamber, and only the pyrolysis of the solid was studied, not the complete combustion (including charring).

3.3.3. Relation with Other Flammability Properties

Further insight into the flammability properties of these degraded materials can be gained through approximate relationships between the heat release capacity, η_c, measured by the MCC and (a) the heat release rate in flaming combustion at a 50 kW/m^2 external heat flux, HRR_{50}, measured with a cone calorimeter, and (b) the limiting oxygen index, LOI%, which is the minimum amount of oxygen required to sustain flaming combustion. Lyon *et al.* [30], have measured such empirical trends, for thin (1–3 mm) thermoset and thermoplastic composites:

$$HRR_{50} = 8\eta_c^{1/2} \quad \text{with a coefficient of determination } R^2 \text{ equal to } 0.41, \tag{1}$$

$$LOI\% = 12 + \frac{4000 \text{ J g}^{-1} \text{ K}^{-1}}{\eta_c}. \tag{2}$$

A value of HRR_{50} equal to 65 kW/m^2 is the maximum allowed by the US Federal Aviation Administration (FAA) for materials in commercial aircraft cabin (Federal Aviation Regulations, FAR 25, [40]). In addition, flammability regimes may be defined in terms of heat release capacity and limiting oxygen index, following the terminology of the Underwriters Laboratory for flammability of plastic materials, UL 94. Lyon *et al.* [30] list four regimes in terms of the heat release capacity and LOI%. For example, materials that will not ignite, i.e., the best case scenario, are characterized by $\eta_c \leqslant 100$ J g^{-1} K^{-1} and $LOI\% > 40$. A self-extinguishing behavior, indicated by V-0/5V in UL 94, occurs for $LOI\% = 30$–40 and $100 < \eta_c < 200$ J g^{-1} K^{-1}. As a rule of thumb, lower rating (less flame retardancy) is shown through increased numbers in the UL 94 'V-' scale.

Results are shown in Table 5 for control and conditioned specimens and all temperatures. Note that the lack of FAA compliance of the materials may depend on the approximate nature of equation (1), and should be viewed with caution, also in light of the UL 94 category for that material. The presence of increased char for the treated samples at high temperature raises the computed LOI% and lowers the flammability risk. Since flammability properties are typically controlled by the polymeric resin, it should not be a surprise that carbon/epoxy appears considerably less vulnerable than the structural epoxy adhesive.

4. Summary and Conclusions

This paper has presented new results for structural adhesive and carbon/epoxy composites exposed to different fluids at room temperature and at high temperatures. These fluids are typical of aerospace operations. There were simplified test conditions (no fluids mixing, no coatings, no prior mechanical damage). In particular, flammability properties of control and conditioned samples were measured with the MCC equipment, or computed from approximate trends available in the literature. The samples' response at high temperature may be affected by the increased amount of char, which provides a barrier against heat and mass transport but is also

Table 5.
Measured heat release capacity, η_c, and computed approximate peak heat release rate in flaming combustion, HRR_{50}, limiting oxygen index, LOI (%), and flammability regimes (computations based on [30])

Treatment	η_c (J g^{-1} K^{-1})	HRR_{50} (kW/m^2)	LOI (%)	Flammability regimes (UL 94)*
Adhesive				
Control	>200	122–139	25.2–29.1	V-2/V-1
Fuel additive	>200 (RT), then	123–133 (RT), then	26.6–29.0 (RT), then	V-2/V-1 (RT), then
	$100 < \eta_c < 200$	92.1–108	33.7–42.2	(V-0/5V) for 30–40
Hydraulic fluid	>200 (RT), then	136–137 (RT), then	25.6–25.8 (RT), then	V-2/V-1 (RT)
	$100 < \eta_c < 200$	85.9–97.0	39.2–46.7	
Jet fuel	>200	123–142	24.7–28.9	V-2/V-1
Water	>200	129–134	26.2–27.3	V-2/V-1
Composite				
Control	$100 < \eta_c < 200$	88.3–94.7	40.5–44.9	
Fuel additive	$100 < \eta_c < 200$	84.6–90.6	43.2–47.7	
Hydraulic fluid	$100 < \eta_c < 200$	81.9–89.6	43.9–50.2	
Jet fuel	$100 < \eta_c < 200$	85.4–89.1	44.3–47.0	
Water	$100 < \eta_c < 200$	86.5–92.2	42.1–46.2	

* Only the four regimes discussed by Lyon *et al.* [30], are given in this table when the appropriate conditions (heat release rate capacity and LOI%) are met.

counterintuitive with respect to the outcome from the TGA, DSC, gravimetric and hardness tests. Additional tests are recommended with the MCC equipment in air to achieve complete combustion, and with a cone calorimeter.

TGA scans indicated a high level of degradation of the adhesive subjected to hydraulic fluid (at high temperature) or fuel additive alone (at all temperatures). Both TGA and DSC results support the use of the currently recommended (not mandatory) post-cure cycle, to increase the durability of the adhesive by alleviating the extent of the degradation.

Within the limits of this study, we demonstrate the susceptibility of uncoated structural adhesive to hydraulic fluid and unmixed fuel additive at high temperatures.

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